



Characterization of zinc lead-borate glasses doped with Fe^{3+} ions: optical, dielectric, and ac-conductivity investigations

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ABSTRACT

The optical, dielectric response, and ac-conductivity properties for six glasses of zinc lead-borate doped with different contents of Fe^{3+} ($\text{Fe}_2\text{O}_3 = 0$ to 10 wt%) have been investigated. UV-Vis spectra in 190–1100 nm wavelength have been carried out. Band gaps for optical energy (E^{Optical}), Urbach's energy (E_U), index of refraction (n), steepness parameter (S), energy dispersion parameter of refractive index (E_d), single-oscillator energy (E_o), the dispersion refractive index (n_o), minimum reflectance wavelength (λ_o), and oscillator strength (S_o) were evaluated. Results reveal that the indirect energy gap varies from 2.57 to 1.01 eV, while the direct energy gap takes values from 2.80 to 1.45 eV. The E_U values change from 0.232 to 0.966 eV for glasses with $\text{Fe}_2\text{O}_3 = 0$ and 10 wt%, respectively. Also, S and λ_o decrease with the enhancement of Fe_2O_3 content. The dielectric response and ac-conductivity of the prepared glasses were investigated by broadband dielectric spectroscopy, BDS, in the frequency range from 0.1 Hz to 10 MHz and at temperatures ranging between 300 and 430 K. Two trends of activation plot have been observed in the conductivity of the samples with low content of Fe_2O_3 . Although these samples show a perfect insulation features, they obey an anomalous behavior at higher temperatures. Therefore, the investigated glasses can be applied in several optical and optoelectronic devices.

1 Introduction

In the last decades, glass materials based on boron oxide (B_2O_3) have gained more attention from several researchers and investigators, due to their unique

interesting physical and chemical characteristics such as good transparency, high transmittance, high chemical durability, low melting temperature, and high thermal stability. These properties lead the borate glasses to be applied in several applications as

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luminescent materials, thermal and mechanical sensors, and as layers for both the opto-electronic and optical devices [1–5]. Introducing lead oxide (PbO) into borate glass systems helps to enhance the optical nonlinearity owing to high polarizability of Pb^{2+} ions in glass networks [6]. On the other hand, association of PbO and B_2O_3 in the glass matrix plays double effect in the glass network: acts as glass former in the case of high boron oxide or acts as network modifier at low concentrations. Therefore, lead-borate glasses show large glass-forming range, which is useful for the manufacturing of structurally and optically different systems [7–9]. For the above reasons, lead-borate glasses were considered as good candidate materials in optoelectronic, photoelectric devices, and in optical switches. Broadband dielectric spectroscopy (BDS) became recently one of the main fruitful techniques for probing dynamic processes and the different mechanisms of the electrical conductivity in advanced glasses and glass ceramics owing to its extensive range of frequency and temperatures [10–14]. There are many studies focused recently on the effect of structure, temperature, and frequency on the electrical properties of conductive glasses [11, 14–20]. The electrical conductivity plays the main role of the variations in all dielectric values (such as permittivity, dielectric loss, electric modulus,...etc.) against frequency and temperature. In cases of ionic conductive glasses, the frequency dependence of the σ' showed a plateau at the lower. The plateau represents the DC-conductivity (σ_{DC}) followed by a power law at higher frequencies. This behavior is now considered as a common feature in many other conducting polymeric systems and hydrogels [21–25]. As the glass is of much higher conductivity, the electrical spectrum is characterized in the lower frequency (or at higher temperature) range by multistep decrease in the real part of conductivity, σ' . This phenomenon is due to the large bulk polarization taking place which is usually called as electrode polarization [15, 20, 26–29]. The electrochemical double layer builds up at the interface between the metallic electrode and the active material (electrolyte) originated from the existence of blocking electrodes which do not let the mobile ions to permit through external circuitry. In addition, there is also the interfacial polarization due to the heterogeneous structure of the considered conductive material. The correlation between both phenomena and the conductivity contribution on the dielectric spectra

usually reflecting the higher rate of permittivity, ϵ' , increases which is very promising in the electrical energy storage technology.

In the present work, the optical, dielectric response, and ac-conductivity characteristics of zinc lead-borate glasses doped with Fe^{3+} ions have been reported. To this end, the UV–Vis spectra for all investigated glasses were carried out in order to evaluate several optical properties. The conductivity of the proposed glasses was performed over wide frequency and temperature ranges. The electrical and dielectric responses of the studied glasses were investigated by broadband dielectric spectroscopy.

2 Materials and measurements

Six glass samples with chemical formula $50\text{B}_2\text{O}_3 \cdot 10\text{ZnO} \cdot (40 - x)\text{PbO} \cdot x\text{Fe}_2\text{O}_3$, where ($x = 0, 1, 2.5, 5, 7.5$ and 10), were prepared formerly by conventional melting method. The starting materials powders boron oxide (B_2O_3) (Sigma-Aldrich) 99.99%, zinc oxide (ZnO) (Winlab) 99.99, lead oxide (Pb_3O_4) (Alfa Aesar) 99.99%, and iron oxide (Fe_2O_3) (Sigma-Aldrich) 99.999 have been mixed very finely and pre-heated at 300°C for 1 h. The resulting powders were then melted inside a porcelain crucible at temperature 1100°C for 20 min and suddenly casted into a stainless steel mold to get the glass discs. After quenching the glass samples were immediately transferred for annealing in a muffle furnace adjusted at 300°C . The preparation steps in detail are described in Ref. [30]. The optical measurements for the proposed glass samples were carried out utilizing JASCO UV–Vis–NIR spectrophotometer model V-570 in the wavelength (λ) range of 190–1100 nm (Table 1).

The electrical and dielectric quantities in the frequency range 10^{-1} – 10^7 Hz were achieved for all investigated glasses utilizing Novocontrol high-resolution alpha dielectric analyzer. This technique is supported by Quatro temperature controllers, using pure nitrogen as a heating agent and assuring temperature stability better than 0.2 K. The measurements were conducted using gold-plated brass electrodes of diameter 10 mm for upper electrode and 20 mm for the lower one in parallel plate capacitor configuration. All measurements were carried out at different temperatures ranging from RT (298) up to 473 K. The complex dielectrics function $\epsilon^*(\omega, T) = \epsilon'(\omega, T) - i\epsilon''(\omega, T)$, where ϵ' is the

Table 1 Codes and chemical composition in samples in the system $(50\text{B}_2\text{O}_3 - 10\text{ZnO} - (40 - x) \text{PbO}) + x\text{Fe}_2\text{O}_3$: $0 \leq x \leq 10$ wt%) glasses [30]

Sample code	Sample chemical composition
$x = 0$	$50\text{B}_2\text{O}_3 - 10\text{ZnO} - 40 \text{PbO} + 0 \text{Fe}_2\text{O}_3$ wt%
$x = 1$	$50\text{B}_2\text{O}_3 - 10\text{ZnO} - 39 \text{PbO} + 1 \text{Fe}_2\text{O}_3$ wt%
$x = 2.5$	$50\text{B}_2\text{O}_3 - 10\text{ZnO} - 37.5 \text{PbO} + 2.5 \text{Fe}_2\text{O}_3$ wt%
$x = 5$	$50\text{B}_2\text{O}_3 - 10\text{ZnO} - 35 \text{PbO} + 5 \text{Fe}_2\text{O}_3$ wt%
$x = 7.5$	$50\text{B}_2\text{O}_3 - 10\text{ZnO} - 32.5 \text{PbO} + 7.5 \text{Fe}_2\text{O}_3$ wt%
$x = 10$	$50\text{B}_2\text{O}_3 - 10\text{ZnO} - 30 \text{PbO} + 10 \text{Fe}_2\text{O}_3$ wt%

permittivity and ε'' is the dielectric loss was obtained. It is equivalent with the complex conductivity function $\sigma^*(\omega, T) = \sigma'(\omega, T) + \sigma''(\omega, T)$ since, $\sigma^*(\omega, T) = i\omega\varepsilon_0\varepsilon^*(\omega, T)$, implying that $\sigma' = \varepsilon_0\omega\varepsilon''$ and $\sigma'' = \varepsilon_0\omega\varepsilon'$ (ε_0 being the vacuum permittivity).

3 Results and discussion

3.1 The optical characterizations

3.1.1 UV–Vis spectroscopy

As mentioned before in Ref. [30], all investigated samples ($x \text{Fe}_2\text{O}_3 = 0$ to 10 wt%) were in glassy state and the color gradient of prepared glass samples is shown in Fig. 1. In order to evaluate the optical properties of the studied glasses, their UV–Vis spectra have been measured in the range of $\lambda = 190$ –1100 nm. Figure 2 depicts the normalized UV–Vis absorption spectra of $50\text{B}_2\text{O}_3 - 10\text{ZnO} + (40 - x)\text{PbO}$ doped with Fe_2O_3 glasses at different values of $x = 0, 1, 2.5, 5, 7.5$, and 10 wt%. From Fig. 2, spectra reveal that there are 3 robust and wide-ranging UV absorption band placed at about 240, 277, and 358 nm, tracked by a broad irregular near-visible band placed about 413 nm [31]. The broad near-visible band focused at about 413 nm shifted towards higher wavelength 655 nm with increasing Fe_2O_3 content. The extended visible absorption band at about 910 nm can be ascribed to the presence of ferric ions (Fe^{3+}) which added to the

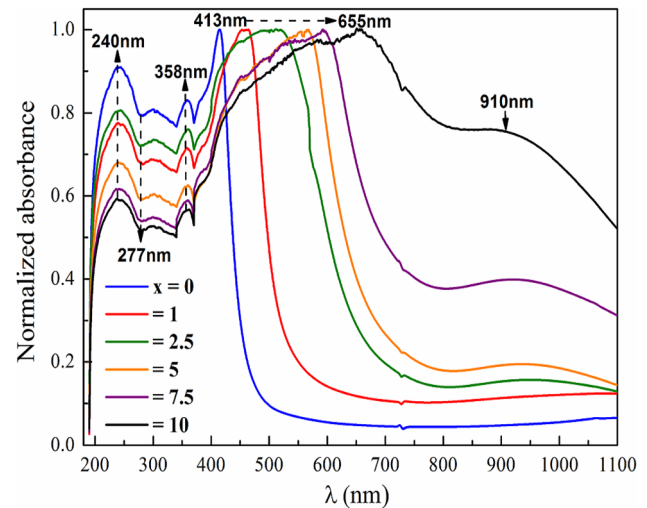


Fig. 2 Normalized absorbance spectra of the investigated glasses.

samples and is ascribed to the transitions ${}^6\text{A}_{1\text{g}}(\text{S}) \rightarrow {}^4\text{A}_{1\text{g}}(\text{G}) + {}^4\text{E}_{\text{g}}(\text{G})$ [32].

3.1.2 E^{Optical} and E_{U}

Direct and indirect band gaps of optical energy for the investigated glasses estimated utilizing their optical absorption coefficient $\alpha(\nu)$ with the help of absorbance (A) and thickness (d) of each sample was calculated utilizing the next relation [33]:

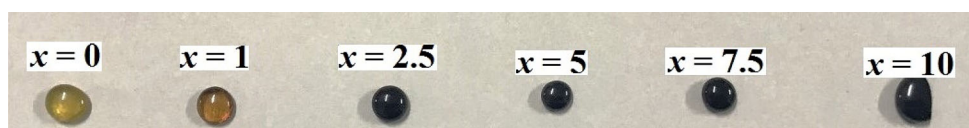
$$\alpha(\nu) = 2.303 \left(\frac{A}{d} \right) = \left(\frac{1}{d} \right) \ln \left(\frac{I_0}{I} \right), \quad (1)$$

where I_0 and I are the strengths of the incident and transmitted beams, respectively. Tauc's [34] and Mott and Davis [35] have been represented for Eq. (1) as

$$\alpha(\nu)h\nu = C(h\nu - E^{\text{Optical}})^m, \quad (2)$$

where C is constant depends on the transition probability, the power m points to the kind of electronic transition ($m = 1/2$ for direct allowable transition and $m = 2$ for indirect one) [35]. In Eq. (2), E^{Optical} refers to the optical band gap energy of the sample. Variation of $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ with $h\nu$ for the investigated glasses is illustrated in Fig. 3a and b. With help of the spectra in Fig. 3a and b, the values of indirect ($E_{\text{Indirect}}^{\text{Optical}}$) and direct ($E_{\text{Direct}}^{\text{Optical}}$) optical energy band gaps can be

Fig. 1 The color gradient of prepared glass samples.



evaluated via extrapolating the straight region of the graphs at the values at which $(\alpha h\nu)^{1/2}$ or $(\alpha h\nu)^2 = 0$. The results reveal that the indirect energy band gaps, $E_{\text{Indirect}}^{\text{Optical}}$ of samples decreased from 2.57 to 1.01 eV, while the direct energy band gaps, $E_{\text{Direct}}^{\text{Optical}}$ decreased from 2.80 to 1.46 eV as the Fe_2O_3 doping increased from $x = 0$ to 10 wt%. The reducing in direct and indirect band gap energies with increasing Fe_2O_3 content may be certified to the Fe faults within the bands, which mark the absorption of incident gamma-photons. The obtained $E_{\text{Indirect}}^{\text{Optical}}$ and $E_{\text{Direct}}^{\text{Optical}}$ values for all studied samples are collected and listed in Table 2.

In the present work, Urbach's energy (E_U) was used to describe the width of band tails as in the following relation [36]:

$$\ln(\alpha) = \ln(\alpha_0) + \frac{h\nu}{E_U}, \quad (3)$$

where α_0 is constant and E_U is the Urbach's energy. Drawing the variation of $\ln(\alpha)$ against $h\nu$ and estimating the inverse of slope for each plot, the corresponding value of E_U can be obtained. Figure 4 shows the plots of $\ln(\alpha)$ against $h\nu$ and Table 2 includes the obtained values of E_U for all the studied glasses. From Fig. 3 and Table 2, one can observe that the E_U values increase as Fe_2O_3 content increases which connected to the creation of localized states in the band gap.

Fig. 3 Variation of $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ with $h\nu$ for the investigated glasses.

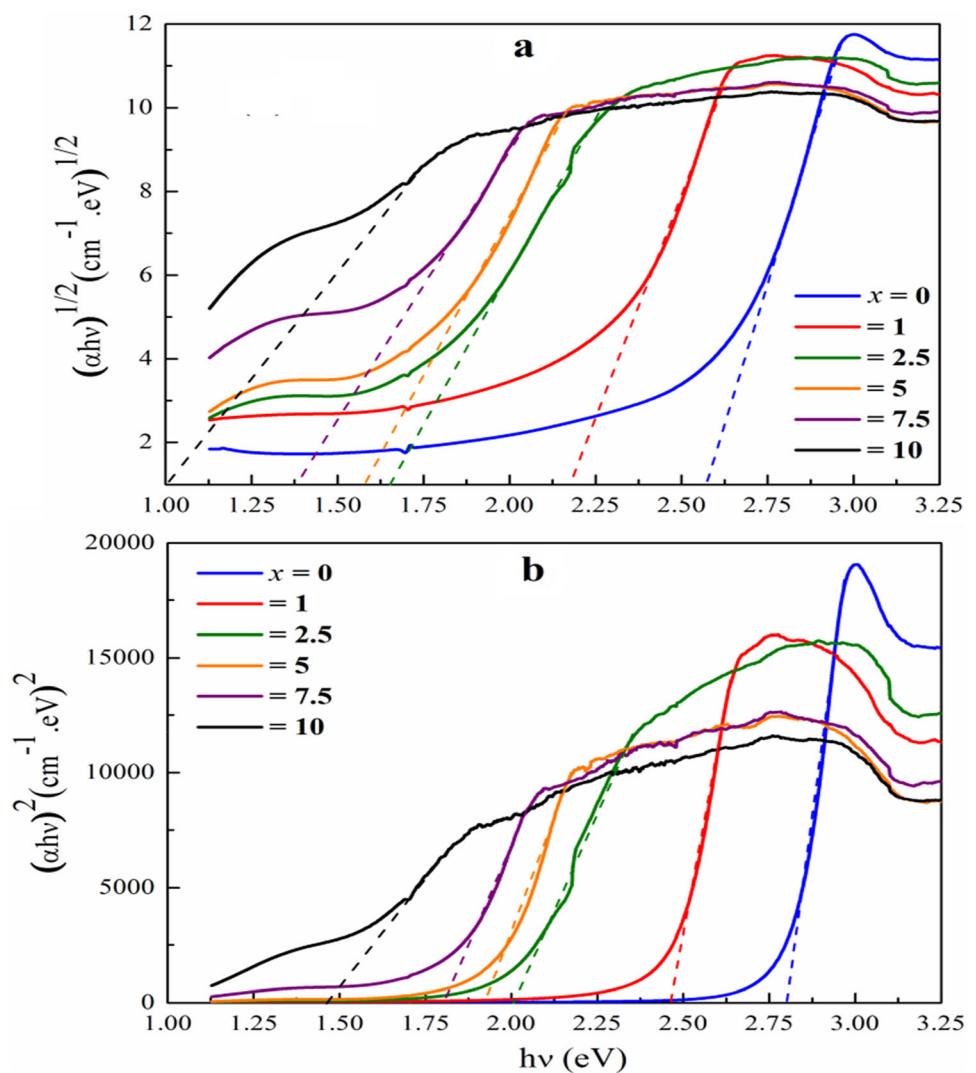
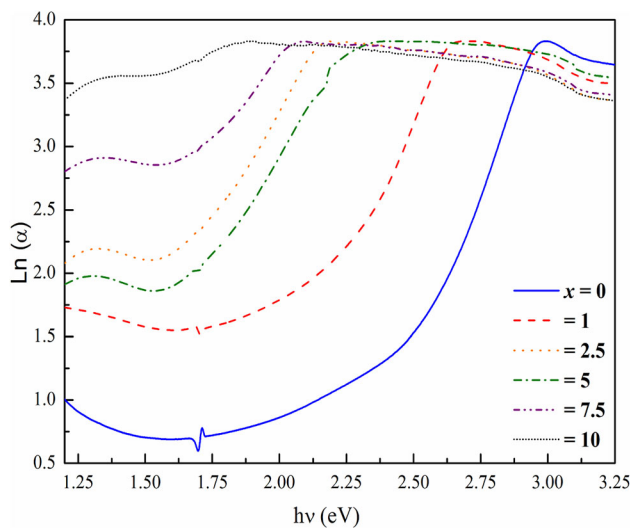


Table 2 E^{Optical} , E_U , S , E_d , E_o , n_o , λ_o , and S_o for the investigated glasses

Sample	E^{Optical} (eV)		E_U (eV)	S	E_d (eV)	E_o (eV)	n_o	λ_o	$S_o \times 10^{-4}$
	Direct $E_{\text{Direct}}^{\text{Optical}}$	Indirect $E_{\text{Indirect}}^{\text{Optical}}$							
$x = 0$	2.80	2.57	0.232	0.111	2.812	3.675	2.99	75.96	13.76
$x = 1$	2.46	2.17	0.264	0.098	2.884	3.354	3.03	71.35	16.06
$x = 2.5$	2.00	1.65	0.382	0.068	3.052	2.851	3.74	66.69	29.20
$x = 5$	1.92	1.57	0.521	0.050	3.984	2.142	4.38	62.35	46.77
$x = 7.5$	1.80	1.36	0.731	0.035	6.604	1.532	4.79	55.35	71.62
$x = 10$	1.45	1.01	0.966	0.026	10.249	1.025	5.05	50.23	97.11

**Fig. 4** $\text{Ln}(\alpha)$ against $h\nu$ for the investigated glass samples.

3.1.3 Steepness parameter (S)

In addition, with help of E_U , the steepness parameter (S) which describes the mechanism of the exciton-phonon (electron-phonon) interactions by which the broadening of the absorption edge for the glass samples is created was calculated via [37]

$$S = \frac{k_B T}{E_U}, \quad (4)$$

where T is the temperature in K° and k_B is the Boltzmann constant. The obtained values of (S) are collected and listed in Table 2, the S value decreases with the increase in Fe_2O_3 content approving the creation of localized states in the band gap [37].

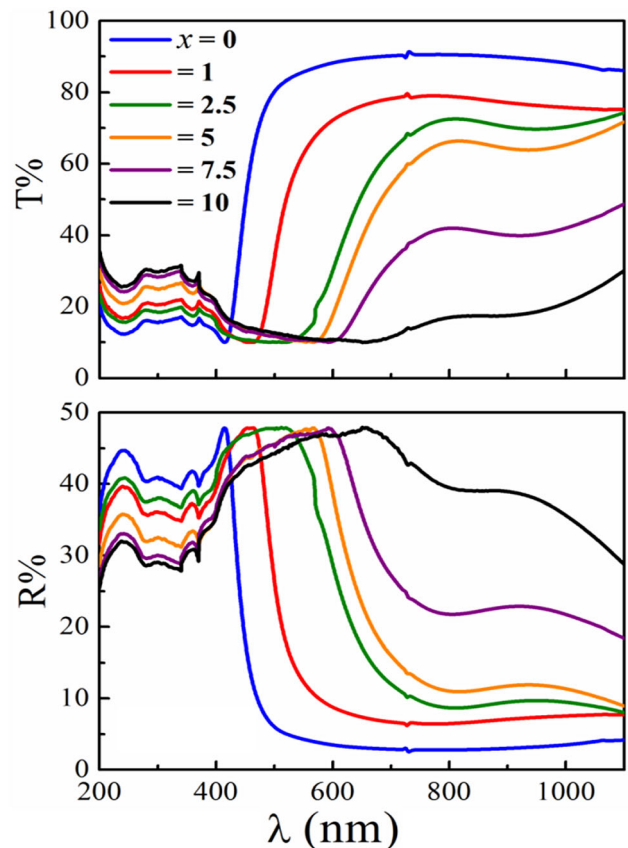
3.1.4 $T(\lambda)$, $R(\lambda)$, and (n)

Dependence of transmittance $T(\lambda)$ and reflectance $R(\lambda)$ measurements for $50\text{B}_2\text{O}_3 \cdot 10\text{ZnO} \cdot (40 - x)\text{PbO}$ glass samples with different concentrations of Fe_2O_3

on λ is plotted in Fig. 4. Plots in Fig. 5 show that the $T(\lambda)$ increases in the ultra-violet region but decreases in the visible region for all studied glasses, while plots of $R(\lambda)$ have an inverse behavior.

The index of refraction (n) for all glasses was evaluated according to [38]

$$n = \left(\frac{1+R}{1-R} \right) + \left(\frac{4R}{(1-R)^2} - k^2 \right)^{1/2}. \quad (5)$$

**Fig. 5** Dependence of $T\%$ and $R\%$ on λ for all investigated glasses.

Here R and k represent the reflectance and the absorption index data, where $k = \alpha\lambda/4\pi$ [38]. The variation of (n) with (λ) for the proposed glasses is depicted in Fig. 5. From Fig. 6, it is seen that the (n) for samples enhances with the increasing Fe_2O_3 content. The values of (n) are considered as high, therefore, the studied glasses can be applied to develop the performance of photovoltaic and optical devices.

3.1.5 (E_d) , (E_o) , (n_o) , (λ_o) , and (S_o)

Additionally, parameter of the energy dispersion of refractive index (E_d) which evaluates the intensity of the interband optical transition for each glass sample can be evaluated utilizing the average of the single-oscillator energy (E_o) through the following relation [39].

$$(n^2 - 1)^{-1} = \frac{E_o}{E_d} - \frac{1}{E_o E_d} (h\nu)^2 \quad (6)$$

Via plotting $(n^2 - 1)^{-1}$ versus $(h\nu)^2$ for each glass sample as shown in Fig. 7, straight lines of each graph intercepts y -axis at a point $= (E_o/E_d)$ and its slope $= (-1/E_o E_d)$, then E_d and E_o can be evaluated. The E_d and E_o are presented in Table 2. The values of (E_o) reduce with increasing Fe_2O_3 content in the glass, i.e., it has the same trend of the optical energy gap, however, the (E_d) has an opposite trend.

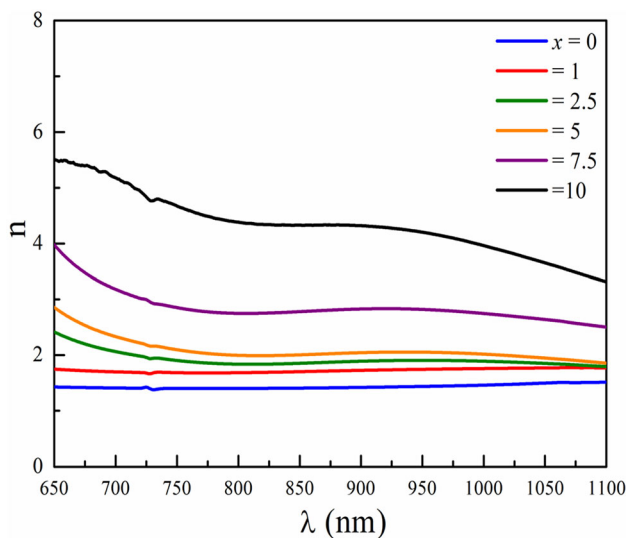


Fig. 6 Dependence of refractive index (n) on λ of the proposed glass samples.

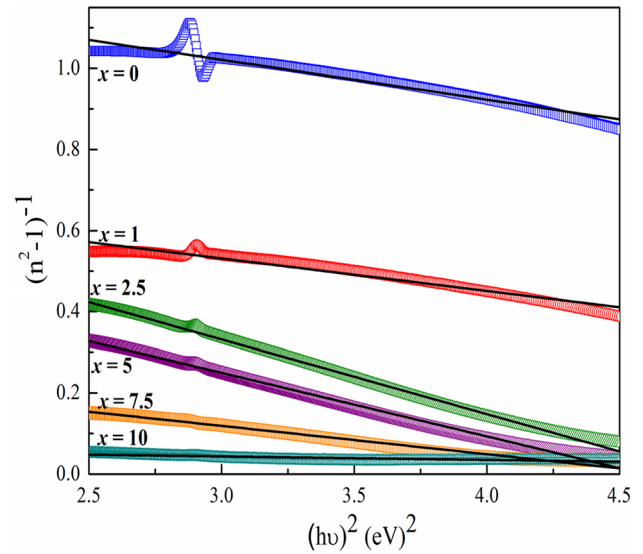


Fig. 7 Variation of $(n^2 - 1)^{-1}$ with $(h\nu)^2$ of the proposed glass samples.

The dispersion refractive index (n_o) at zero energy photon (static refractive index) is calculated with help of the values of E_o and E_d as in Eq. (7) [39] and are listed in Table 2:

$$n_o^2 = \left(1 + \frac{E_d}{E_o}\right) \quad (7)$$

The values of n_o for the studied glasses increase with increasing Fe_2O_3 concentration.

Finally, the wavelength values at a minimum reflectance (λ_o) for the studied glasses were evaluated utilizing Eq. (8) by drawing $(n^2 - 1)^{-1}$ versus λ^{-2} as in Fig. 8 according to Moss model [40]:

$$\left(\frac{n_o^2 - 1}{n^2 - 1}\right) = 1 - \left(\frac{\lambda_o}{\lambda}\right)^2 \quad (8)$$

The average oscillator strength (S_o) can be evaluated with help of (λ_o) for all samples via Eq. (9) [39, 41]

$$S_o = \frac{(n_o^2 - 1)^2}{\lambda_o^2} \quad (9)$$

The obtained values of (λ_o) and (S_o) for each glass sample are listed in Table 2. It is clear that the (λ_o) decreases while the (S_o) increases with increasing Fe_2O_3 content.

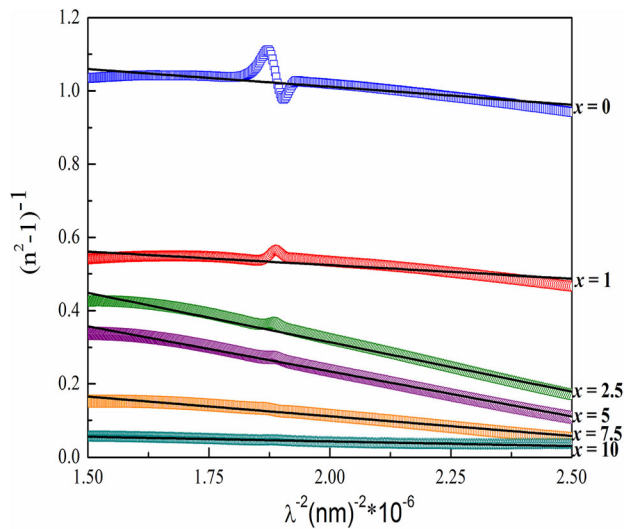


Fig. 8 Variation of $(n^2 - 1)^{-1}$ with $(\lambda)^{-2}$ of the proposed glass samples.

3.2 Dielectric and electrical and investigations

The real part of the complex permittivity, ϵ' , for the studied glasses at ambient room temperature is depicted against frequency in Fig. 9. No remarkable effect of the frequency on the permittivity is noticed here reflecting the stability nature of the considered glasses. Also, the permittivity shows a very slight increase from 20 to 24 with increasing the concentration of Fe_2O_3 up to 10 wt % as shown on the inset

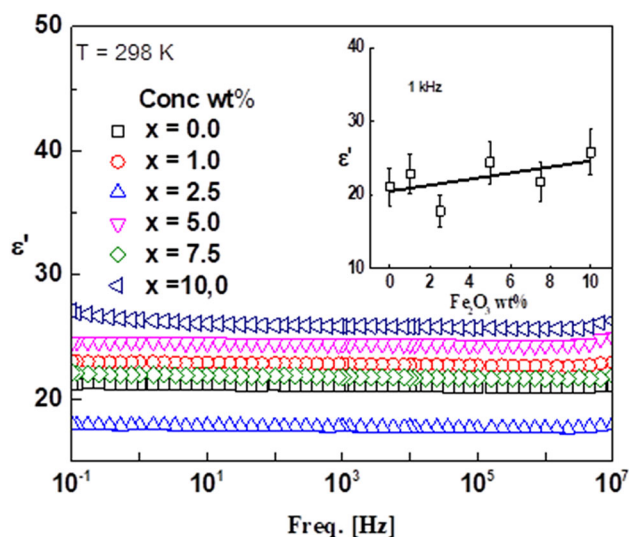


Fig. 9 The permittivity, ϵ' presented against frequency at RT for all samples under investigations. The inset shows the effect of concentration on the permittivity.

of the figure. This gives the indication that the investigated glasses are dielectrically stable at room temperature against frequency of the external applied electric field and the doping with Fe_2O_3 .

Also, the inset of the figure represents the effect of the Fe_2O_3 doping on the permittivity as determined at RT and frequency 1 kHz. In all cases a very low change of the permittivity could be seen here. This confirms, once again, the dielectric stability of the investigated glasses at ambient temperature. The measured permittivity, ϵ' , and ac-conductivity, σ' , are illustrated graphically, as a function of measuring temperature at spot frequency point 1 kHz, in Fig. 10 for the two glass samples ($x = 1$ and 5) as a representative example. In this context, we will consider the real part of electric conductivity, σ' , as the ac-conductivity, σ_{ac} . Figure 10 shows linear increase of ϵ'

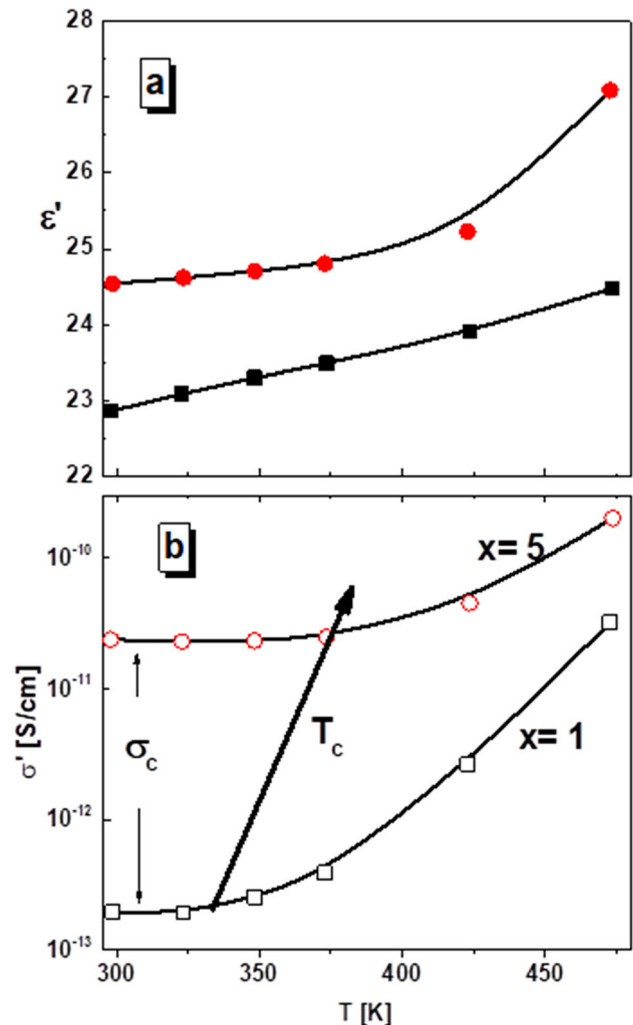


Fig. 10 The permittivity, ϵ' (a) and ac-conductivity, σ' (b) as presented against temperature at 1 kHz for $x = 1$ and 5 glasses.

with increasing temperature for the sample ($x = 1$). This is due to the increase of the mobility of the charge carriers with heating, however, the rate of change is remarkably increasing and deviated from linearity in the case of the sample ($x = 5$) at relatively higher temperatures. The abrupt increase of permittivity and hence of the ac-conductivity is attributed to the ferric ions (Fe^{3+}) which are added to the samples as temperature rose. Even though it is clear that the two glasses show a very good dielectric stability against heating since the increase of temperature from 300 to 475 is responded by increase of permittivity from 23 to 24 for the sample $x = 1$ and from 24.5 to 27 for $x = 5$, this may reflect the insulation features of the glasses under considerations. The real part of the complex conductivity σ' is characterized on the low temperature side by a plateau-like behavior. The conductivity at that lower temperature range is constant (σ_c) and characterizes the structure of the investigated glass samples.

The characteristic temperature T_c , at which dispersion sets in and turns into a power law at higher temperatures, seems to be increased as σ_c . This behavior is somewhat like the behavior of the frequency dependence of σ' for many conductive systems [42–45]. One has to notice that, σ_{ac} , in all cases and at all considered measuring temperatures as low as pico S/cm to nano S/cm which is in the range of insulating materials.

Figure 11 illustrates graphically the frequency dependence of permittivity, ϵ' , for the highly Fe_2O_3 -doped glass ($x = 10$) at different temperatures ranging from 25 to 200 °C. The figure shows that the value of permittivity attains a constant minimum value at

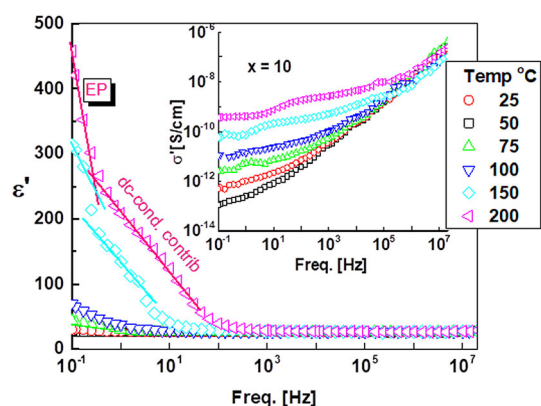


Fig. 11 The real part of permittivity, ϵ' , as presented against frequency at various temperatures as indicated for the sample ($x = 10$). Inset shows the debate plot of ac-conductivity.

higher frequencies collapsed for all considered temperatures. This could be explained by the lag of the polarizations' alteration behind that of the applied electric field. The values of, ϵ' , split up by decreasing the frequency according to the measuring temperatures. The other prepared glass compositions of high doping of Fe_2O_3 show analogous behavior. Two mechanisms are behind the abrupt increase at lower frequencies in values of permittivity, ϵ' could be characterized by the two trends observed here. The first one originated from the accumulation of charge carriers at the interfaces: (a) between the electrodes and the material, due to the presence of blocking electrodes which do not allow the mobile ions to pass through external circuitry, this is called electrode polarization; (b) at the interfaces between different materials in heterogeneous structure and is produced by the separation of mobile positively and negatively charged particles under an applied field, which form positive and negative space charges in the bulk of the material. It is usually called space charge or Maxwell–Wagner–Sillier, MWS, polarization. The correlation between them causes the abrupt increase of permittivity as the frequency decreases making the investigated glass promising for energy storage technology. The second trend is of lower rate of change and is accompanied by the hopping mechanism of charge carriers' transportations and correlated to the dc-conductivity. The latter is characterized by plateau-like behavior on σ' representation as shown in the inset of the figure.

In order to report the influence of frequency, temperature, and composition on the ac- and dc-conductivity, the frequency dependence of σ' of three different samples is depicted at two different temperatures in Fig. 12. Figure 12 shows linear decrease of σ' with decreasing frequency at RT (298 K) for the sample of lower Fe_2O_3 ratio content (1 wt%) that is coincident with that of the Fe_2O_3 -free sample. This behavior is the common feature of the perfect insulator glasses and it has a value of σ' in the order of $[4 \times 10^{-15} \text{ S/cm (femto Siemens per cm)}]$ at 0.1 Hz. As the ratio of Fe_2O_3 increases to 10 wt%, this value tends to be 10^{-13} , i.e., 1.5 order of magnitude higher. However, the increase of measuring temperature up to 475 K enhances the dc-conductivity to about 3.5 decades higher for all investigated samples. By conducting more inspection of the figure at relatively higher temperature, two frequency-independent plateau regions were noticed. The plateau region at

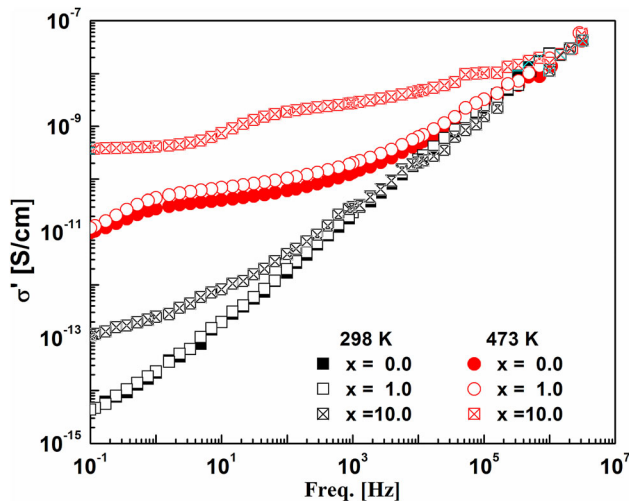


Fig. 12 The real part of conductivity, σ' , as presented against frequency at two selected temperatures and for three selected samples as indicated.

low frequencies corresponds to the accumulation of charge carriers at the surface of the electrode–electrode polarization. It shifts remarkably towards lower frequencies as the temperature and/or the ratio of Fe_2O_3 decreases to be out of the considered window of frequency. The other plateau at intermediate frequencies correlates to the long-range defect migration of impurities that exhibits the dc-conductivity. The bend-like behavior shown at high frequencies highly corresponds to the structural relaxation process (α -process) that correlate with the interfacial polarization.

Figure 13 illustrated the temperature dependence of $\sigma@1\text{ Hz}$ which could be considered as the dc-conductivity σ_{dc} at least for the semi- and highly conductive glasses. Figure 13 confirmed, once again, the insulation feature at relatively lower temperatures for the samples of Fe_2O_3 up to 0–5 wt%. There are two trends according to the range of temperature under consideration. The conductivity increases with low rate up to 70° C and then the rate tends to be much higher. The sample $x = 5$ has the lowest values of conductivity that attributed previously to the blocking effect of Fe_2O_3 on flow of charge carriers [46]. The activation plot of the two trends for the samples $x = 0$ –5 and of the two samples of higher Fe_2O_3 ratios (7.5 and 10 wt %) follows an Arrhenius relation which reads [47, 48]

$$\sigma_{\text{dc}} = \sigma_{\infty} \exp\left(-\frac{E_A}{K_B T}\right), \quad (10)$$

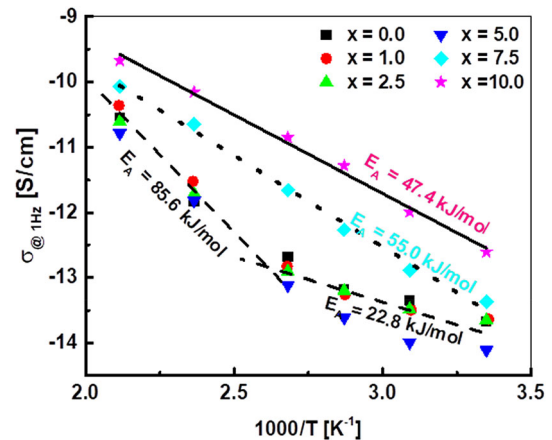


Fig. 13 Arrhenius plot of the real part of conductivity, σ' , at one spot frequency point 1 Hz for $x\text{Fe}_2\text{O}_3$ ($x = 0, 1, 2.5, 5, 7.5$, and 10 mol%) glasses.

where E_A is the activation energy, K_B is the Boltzmann's constant, and σ_{∞} the dc-conductivity in the high-temperature limit. The calculated values of activation energy for all the samples are also shown in the plot for different glass compositions, which is calculated using Arrhenius temperature dependence. It can be observed that σ_{dc} is increasing, and E_A is decreasing for the sample of 10 wt% Fe_2O_3 in comparison with that of 7.5 wt %. This can be explained on the basis of the fact that the ferric ions (Fe^{3+}) which added to the samples have higher mobility which may result in the increase in conductivity and decrease in activation energy with increase in Fe_2O_3 content. The abrupt increase of the conductivity at relatively higher temperatures range for the glasses $x = 0$ –5 wt% can be attributed to the increase of the ions' mobility. However, the accompanied increase of the activation energy does not agree with that view since the increase of E_A should be due to something hindered the mobility which in turn decreases the conductivity which is not the case. Further work should be done in order to modulate and clarify that anomalous behavior.

4 Conclusion

The optical, electrical, and dielectric properties for six glasses of zinc lead-borate doped with different contents of Fe^{3+} with chemical formula $50\text{B}_2\text{O}_3 + 10\text{ZnO} + (40 - x)\text{PbO} + x\text{Fe}_2\text{O}_3$: $x = 0, 1, 2.5, 5, 7.5$, and 10 wt% have been investigated. UV–Vis

spectra in 190–1100 nm wavelength have been carried out. Results reveal that the indirect energy gap varies from 2.57 to 1.01 eV, while the direct energy gap takes values from 2.80 to 1.45 eV of the proposed glasses. Urbach's energy (E_U) values change from 0.232 to 0.966 eV for glasses with $\text{Fe}_2\text{O}_3 = 0$ and 10 wt%, respectively. The wavelength values at a minimum reflectance (λ_o) decrease with enhancement of Fe_2O_3 content. The average of the single-oscillator energy (E_o) decreases from 3.675 to 1.025 for glasses with 0 to 10 wt% of Fe_2O_3 content. The energy dispersion parameter of refractive index (E_d) increases from 2.812 to 10.249 for glasses with 0 to 10 wt% of Fe_2O_3 content. The investigated glasses are dielectrically stable at room temperature against frequency of the external applied electric field and doping with Fe_2O_3 . The (σ_{ac}) in all cases and at all considered measuring temperatures as low as pico S/cm to nano S/cm which is in the range of insulating materials. The conductivity at that lower temperature range is constant (σ_c) and characterizes the structure of the investigated glass samples. The increasing of measuring temperature up to 475 K enhances the dc-conductivity to about 3.5 decades higher for all investigated samples.

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